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14. ABSTRACT High nitrogen compounds are the focus of advanced energetic material research aimed at future needs in the area of advanced explosives and propellants. One method of building nitrogen rich molecules consists of using a core heterocycle, e.g. a tetrazole, and nitrogen containing pendant groups like amines and azides. Hydrazine and its derivatives are widely used as propellants and a combination of two energetic compounds, i.e. hydrazines and tetrazoles, might provide materials with advantageous properties for energetic applications. Instead of coupling the hydrazine moiety directly to the tetrazole ring, we decided to incorporate an alkyl spacer which can help to increase thermal stability and lower the sensitivity towards impact and friction.					
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16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  SAR	18. NUMBER OF PAGES  25	19a. NAME OF RESPONSIBLE PERSON Stefan Schneider
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## **Synthesis and Characterization Of 5-(hydrazino-alkyl) tetrazoles**

**ACS San Francisco 2014**

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Ionic Liquids (ILs) group  
ERC/ AFRL/RQRP  
Edwards AFB, CA**



## *Objectives*



- Development and fielding of new energetic materials for advanced chemical propulsion in space and missile applications
- Design energy dense, ionic liquids with very fast (hypergolic) ignition response

Anion control hypergolic activity,

Cation influences ignition delay times (IDs)

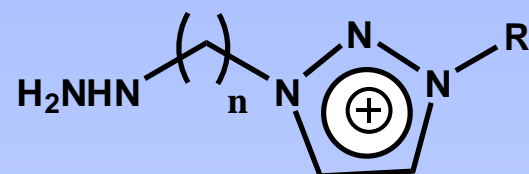
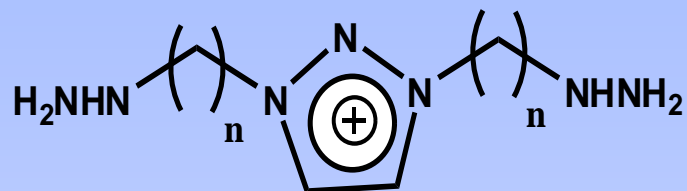
Combining energetic functional groups such hydrazines and heterocyclic rings such as tetrazoles, triazoles etc.



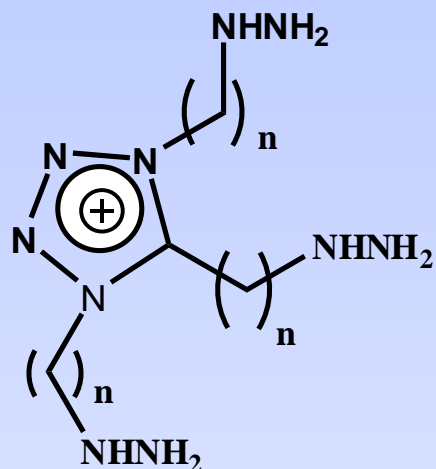
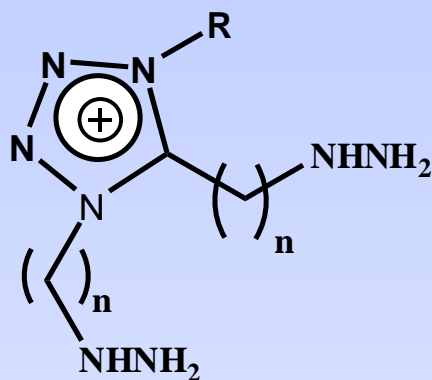
## *Combination of energetic functional groups and heterocycles*



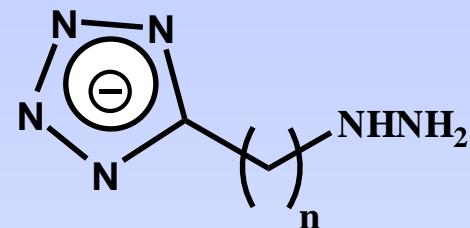
### Triazolium cation



### Tetrazolium cation

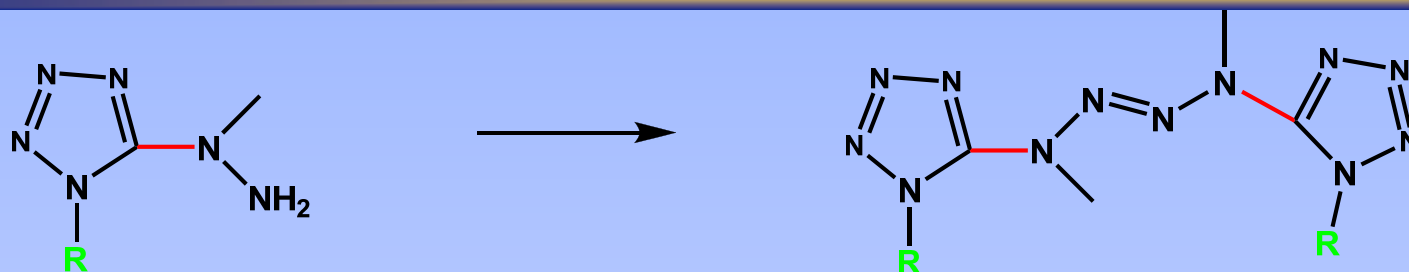


### Tetrazolate anion

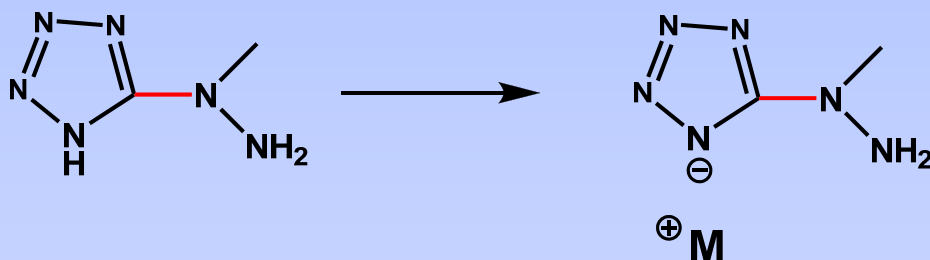




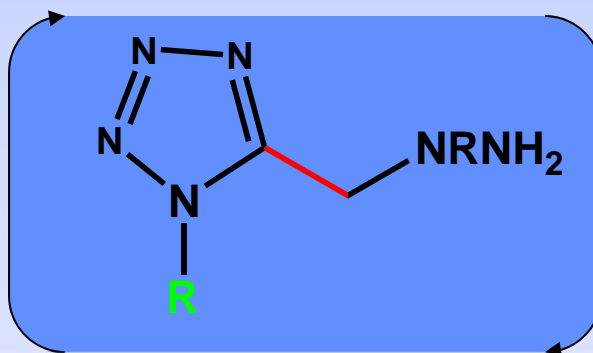
## Reported 5-hydrazino -1H - tetrazoles



T. M. Klapötke, et al *J. Org. Chem.*, **2009**, 2460



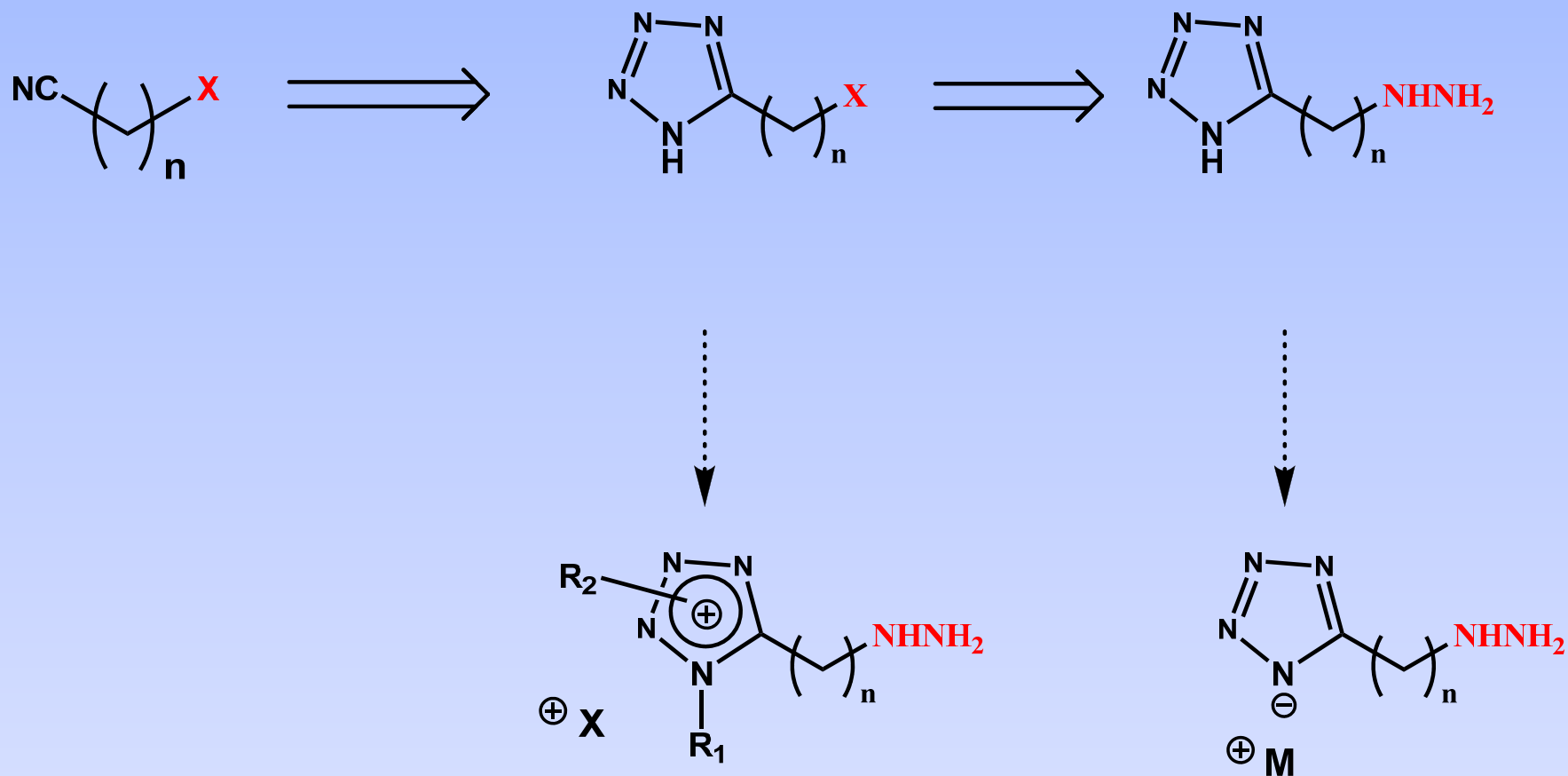
Si-P Pang, et al, *J. Mater. Chem. A.*, **2013**, 6776



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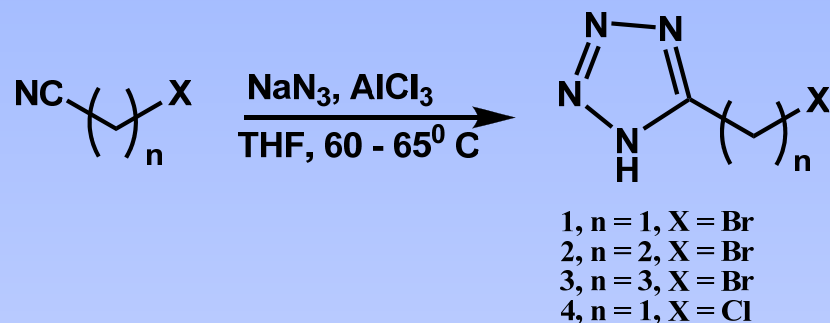
## Targeted molecules



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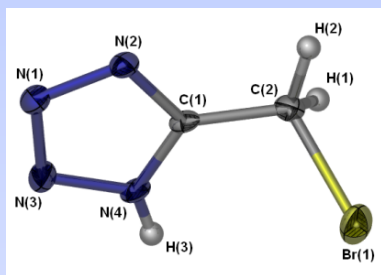


## Synthesis of 5-(halo-alkyl)-tetrazoles

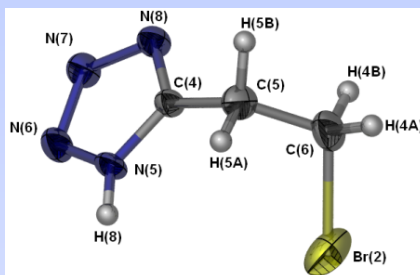


*Russ. J. Org. Chem.*, 2006, 1049

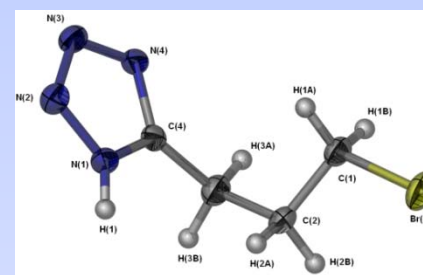
### Single X-ray crystal structures of 5-(halo-alkyl)-Tetrazoles 1- 3



1



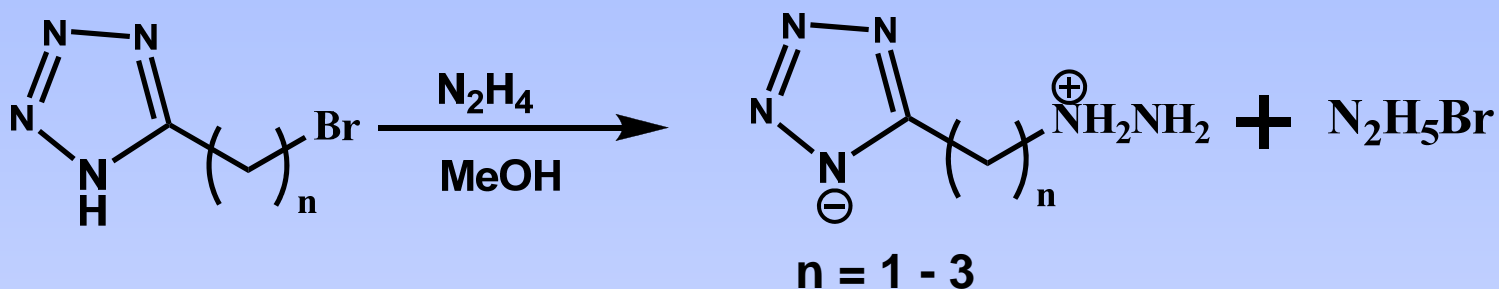
2



3



## Synthesis of 5-(hydrazino-alkyl)-tetrazoles



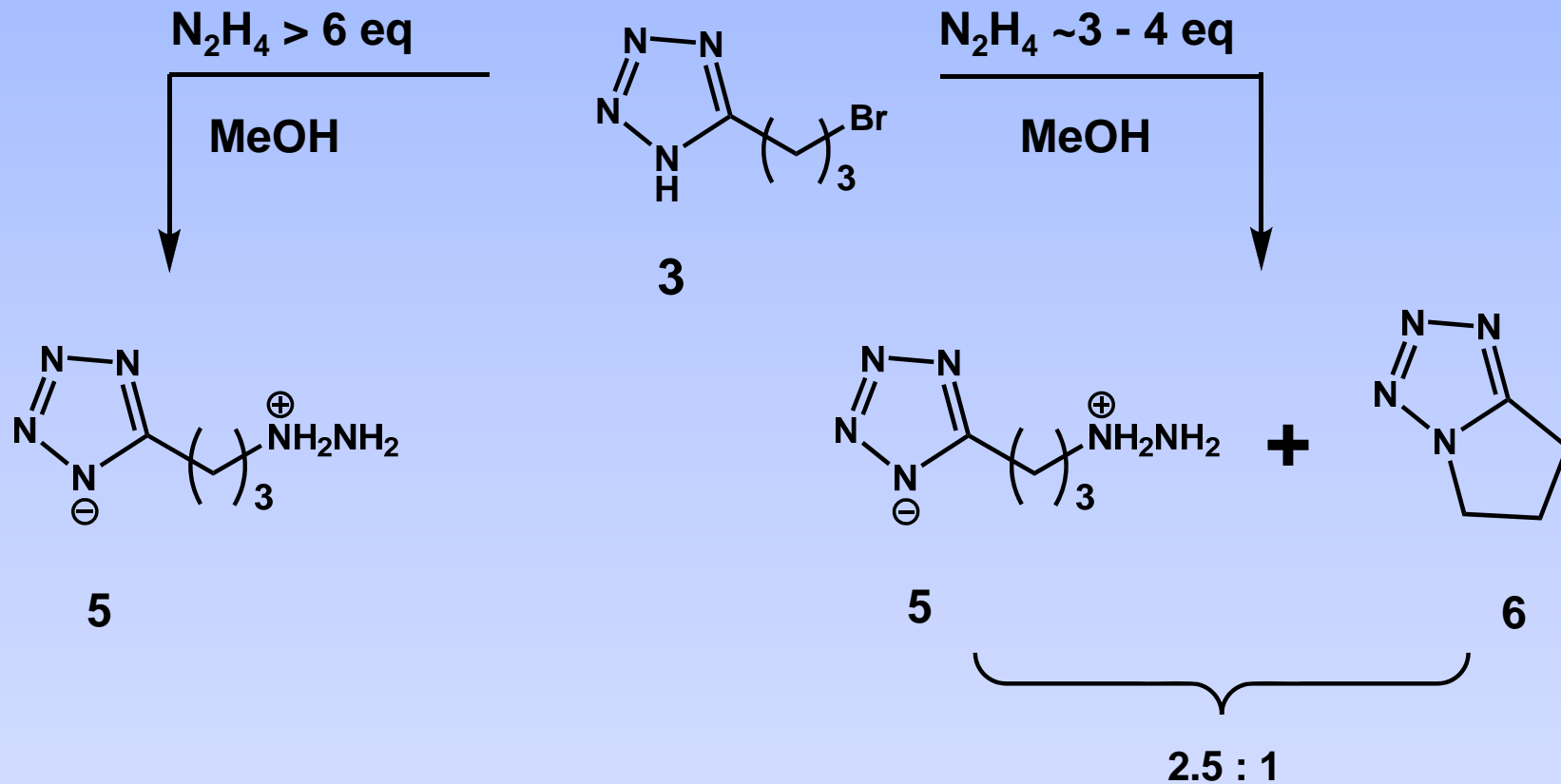
Compound	Solubility				Physical state
	H <sub>2</sub> O	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHOH	
n = 1	soluble	Sparingly soluble	insoluble	Insoluble	Viscous oil
n = 2	soluble	soluble	insoluble	Insoluble	Viscous oil
n = 3	soluble	soluble	sparingly soluble	soluble	Viscous oil

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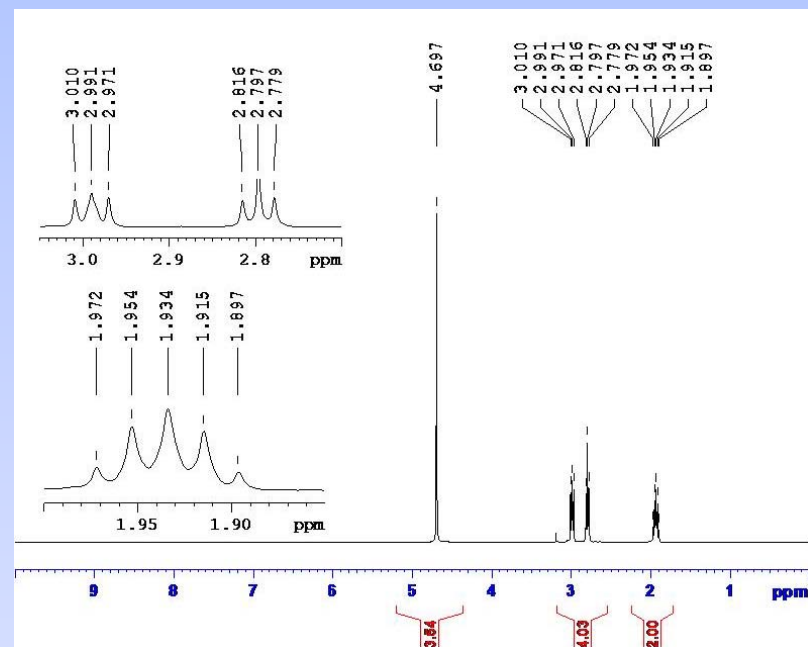
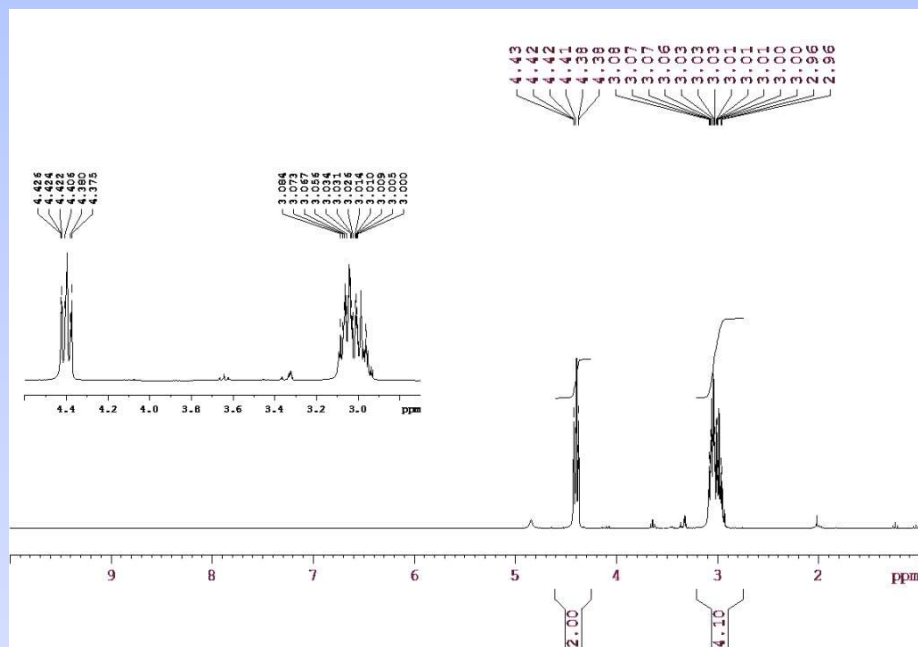
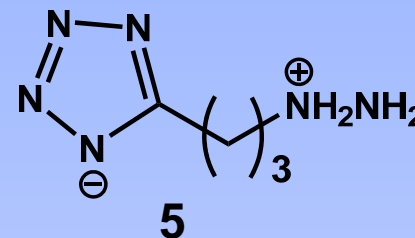
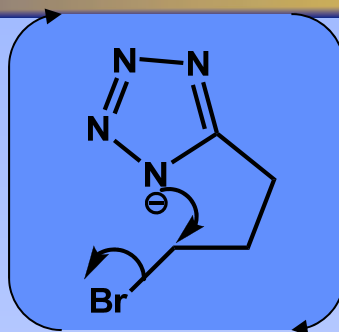
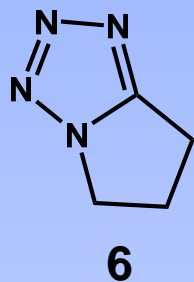


## Synthesis of 5-(hydrazino-propyl) tetrazole



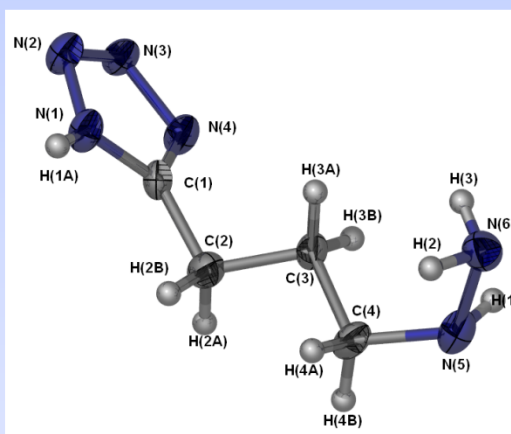
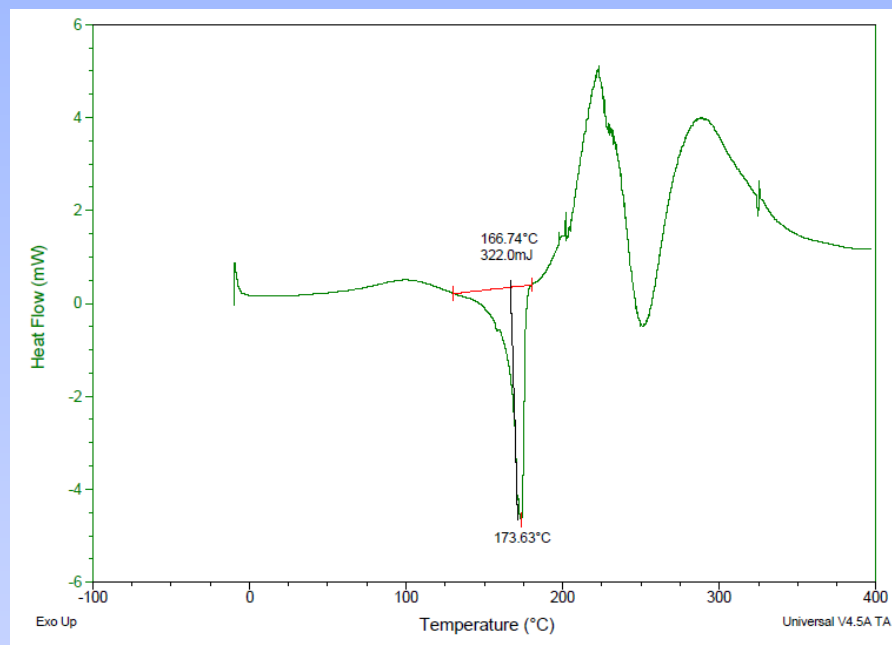
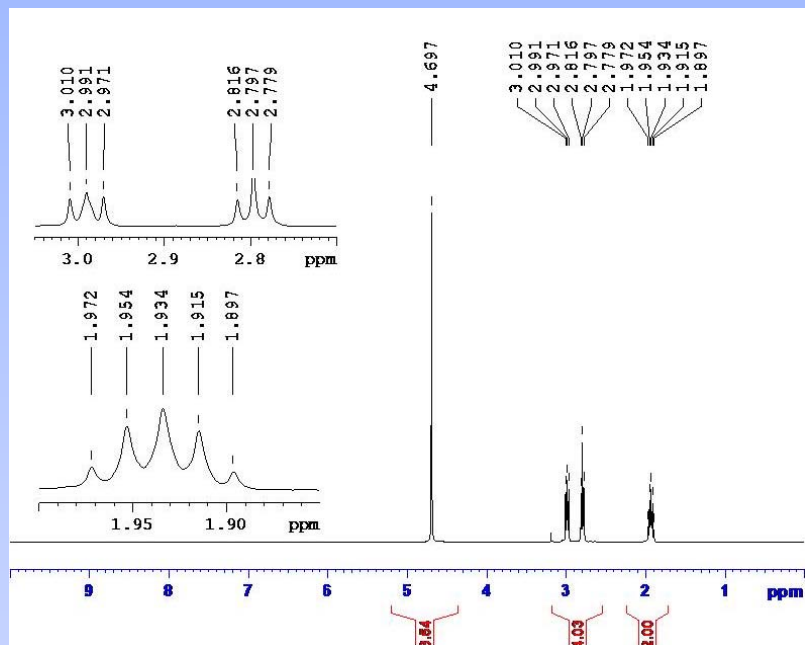


# $^1\text{H}$ NMR spectra of 1, 5-trimethylene tetrazole (6) and 5-(hydrazino-propyl) tetrazole





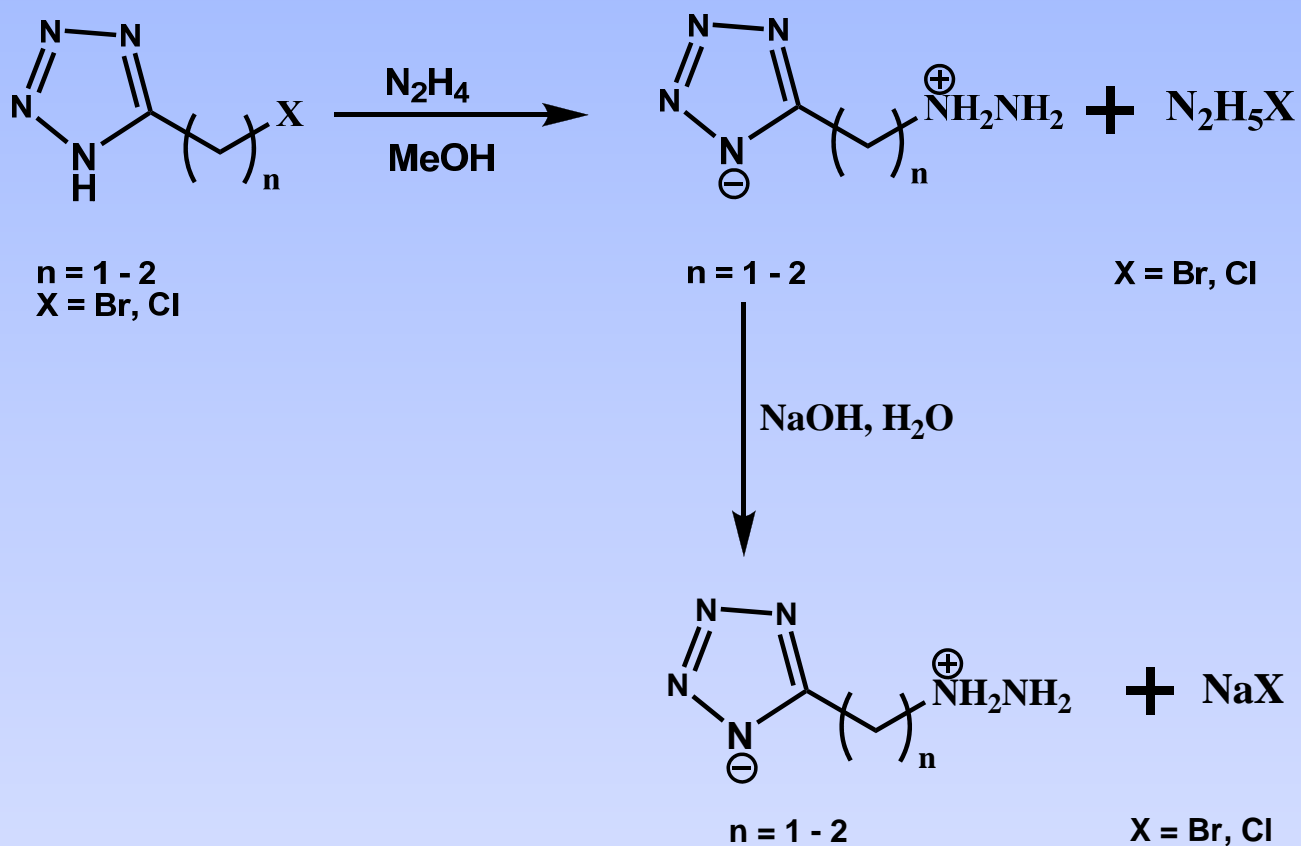
## *DSC, Single crystal X-Ray structure and $^1\text{H}$ NMR spectrum of 5-(hydrazino-propyl) tetrazole*



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## *Synthesis of 5-(hydrazino-alkyl) tetrazole*



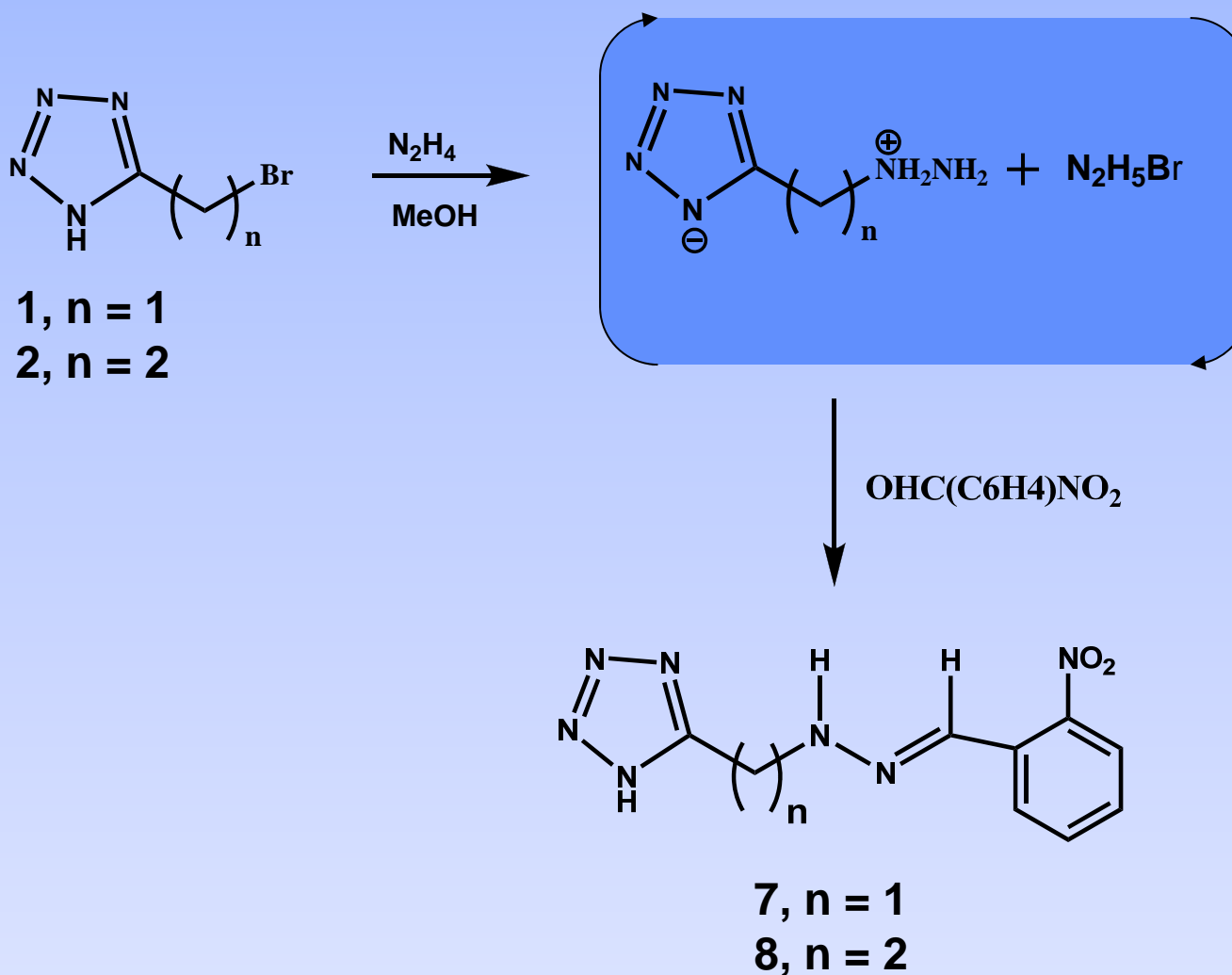
**Difficult to separate due to poor solubility of the zwitter ions**

Unprecedented in the literature

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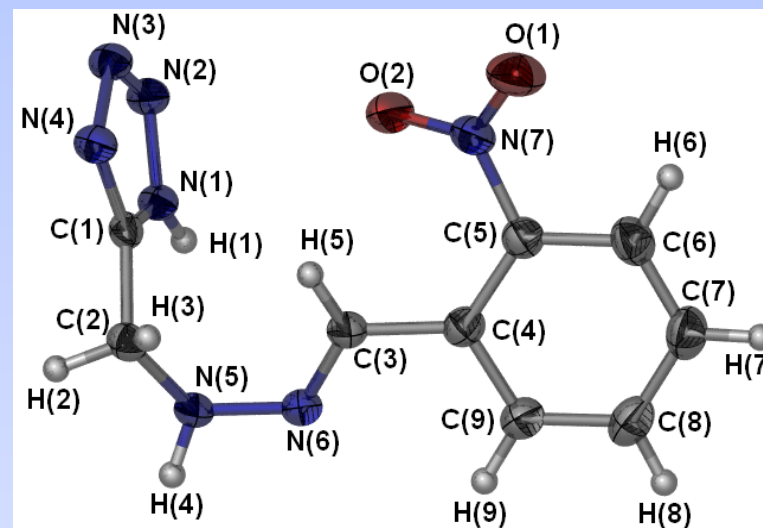
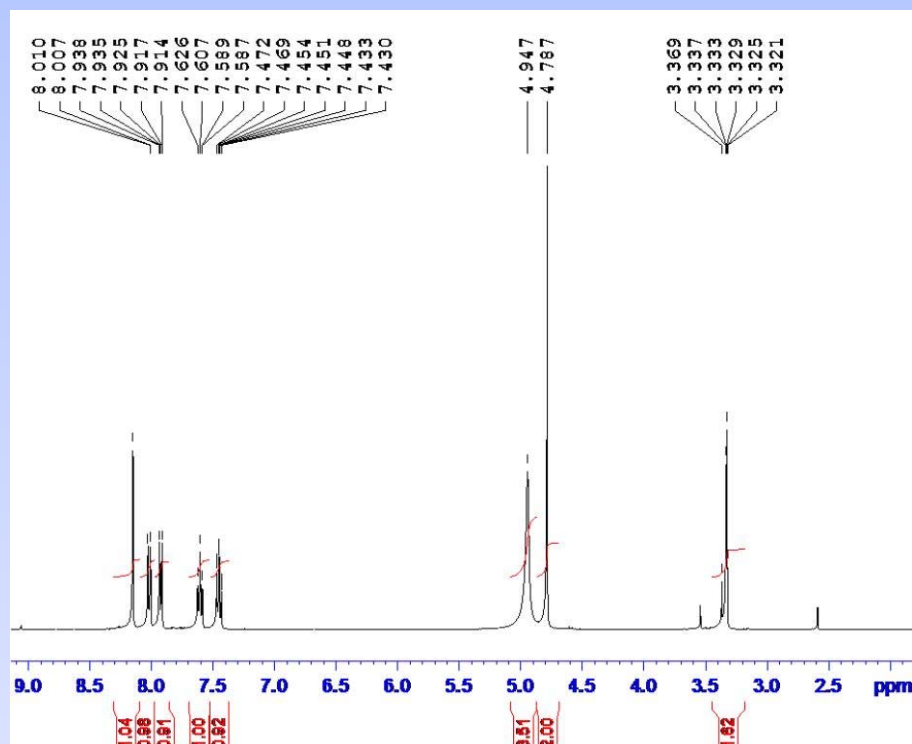


## Reactions of crude 5-(hydrazino-alkyl)tetrazoles with 2-nitrobenzaldehyde





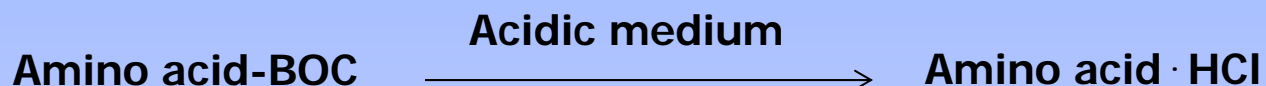
## Single crystal X-Ray structure and $^1\text{H}$ NMR spectrum of hydrazone 7



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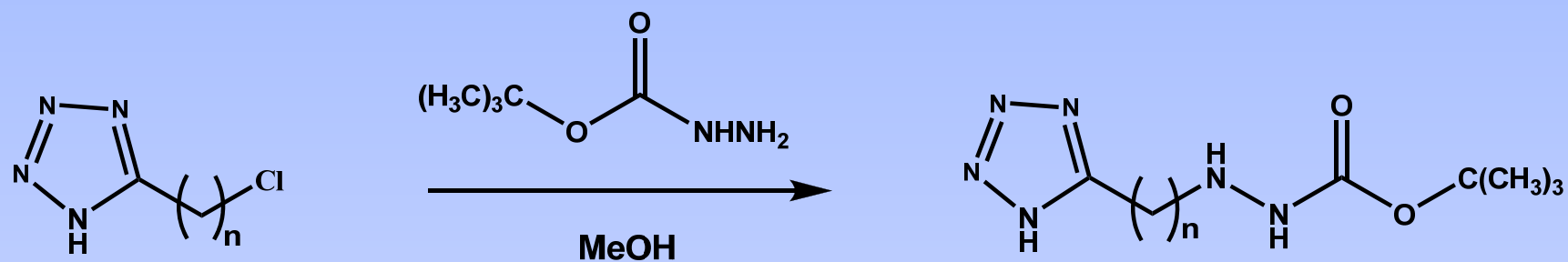
## *Synthesis of 5 - (hydrazino - alkyl) tetrazole via BOC hydrazine*



- Address solubility issues
- Solid state structures of hydrochloride salt
- Hydrochloride salt as substrate for metathesis reaction with energetic anions e.g [NO<sub>3</sub>], [N<sub>3</sub>], etc.



## Synthesis of 5 - (hydrazino - alkyl) tetrazole via BOC hydrazine



9,  $n = 1$   
10,  $n = 2$

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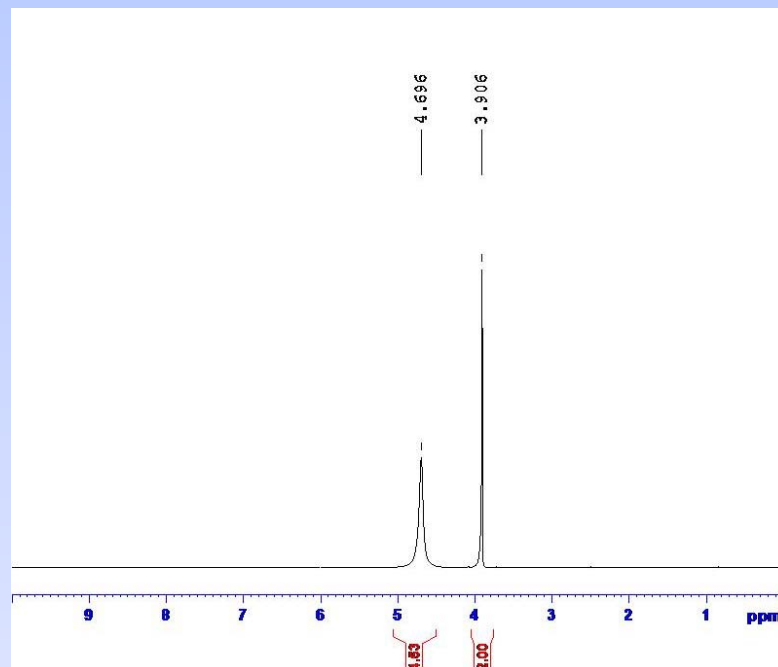
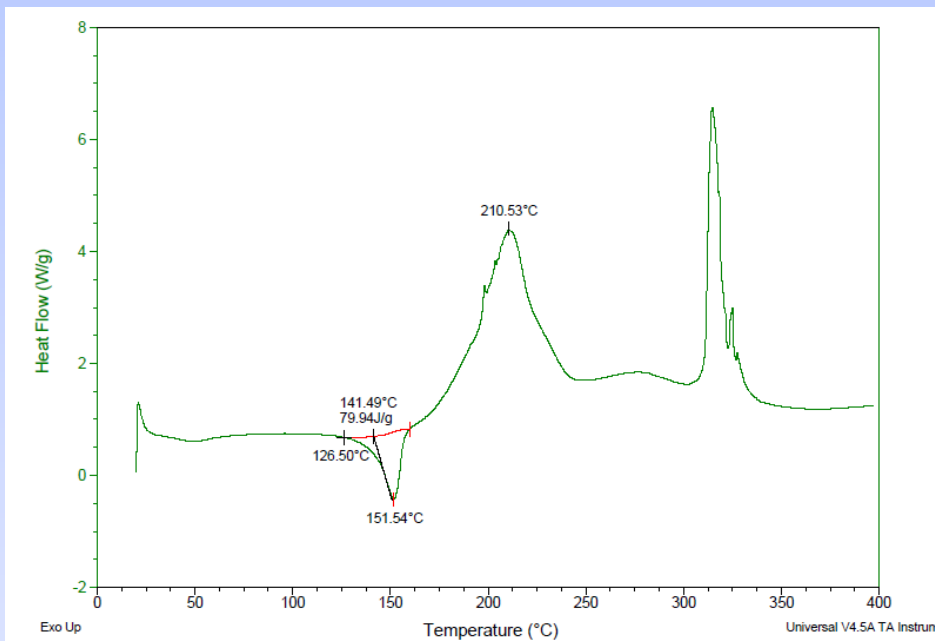




## Removal of BOC protecting group



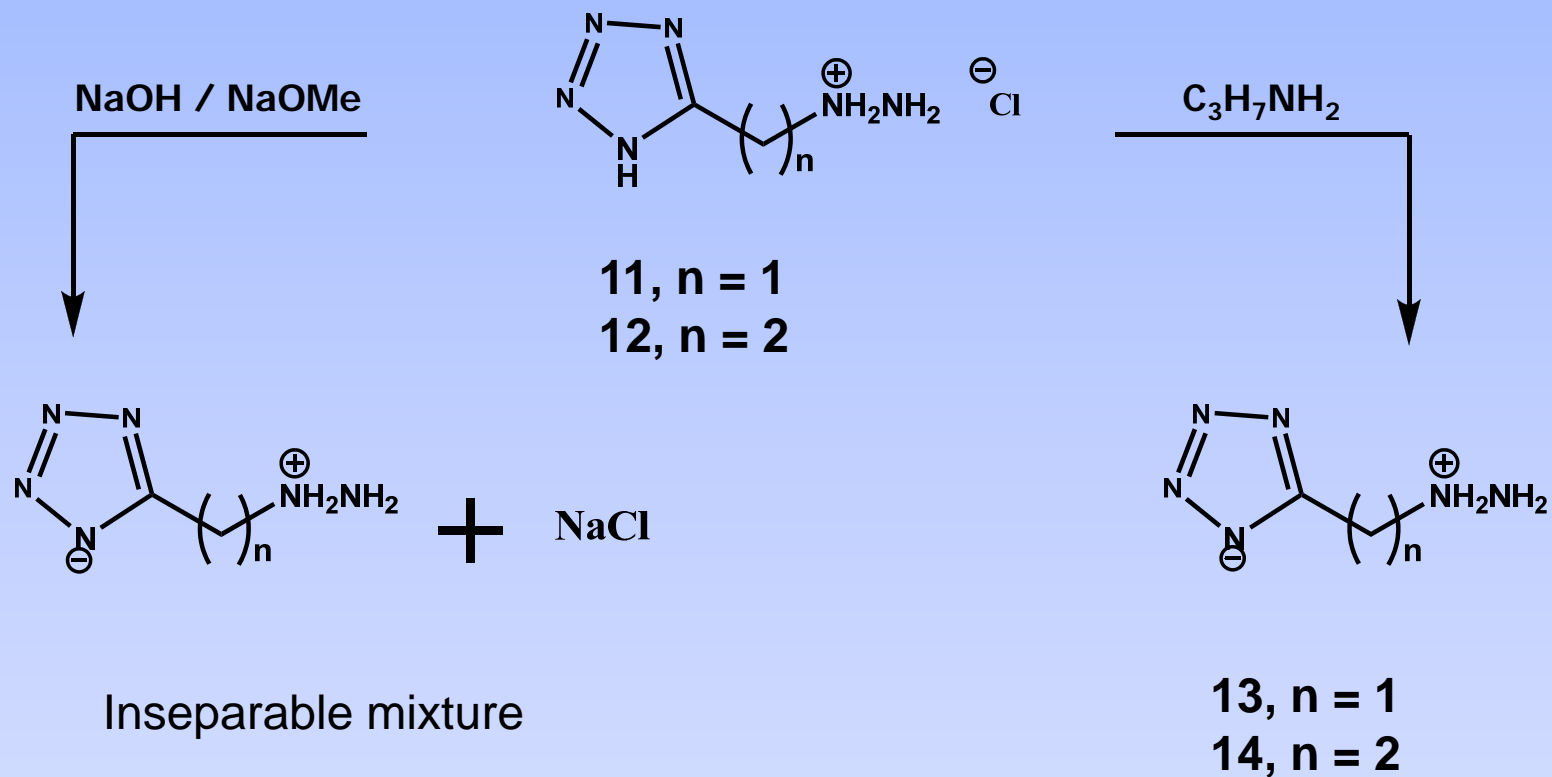
### <sup>1</sup>H NMR and DSC of 5-(hydrazino-methyl)tetrazole mono-hydrochloride 11



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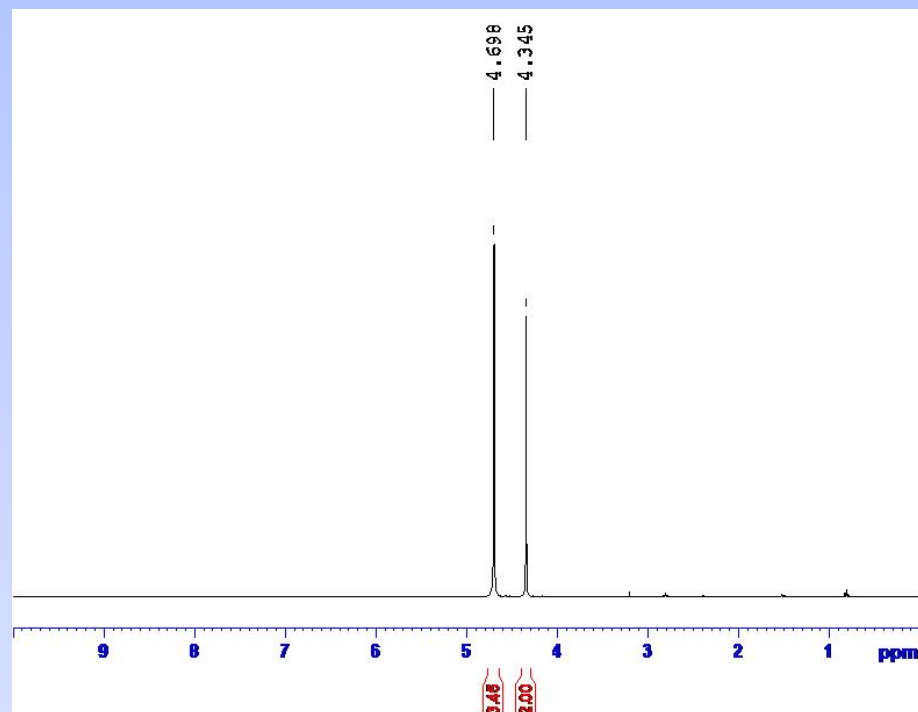
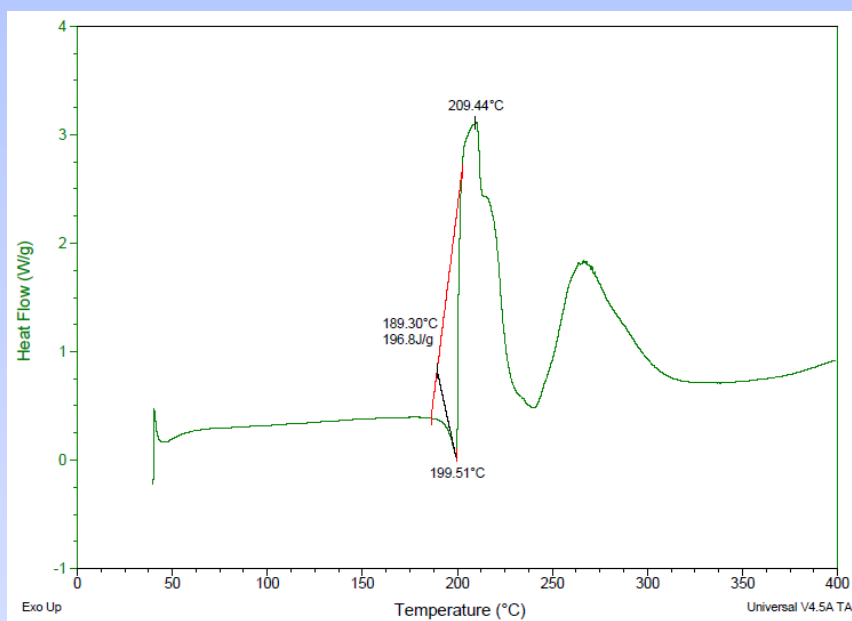
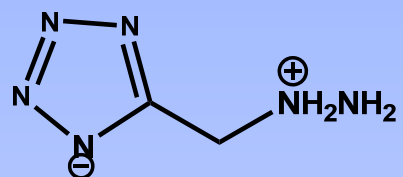


## Neutralization of 5-(hydrazino-alkyl)tetrazole mon-hydrochlorides salts 11 and 12





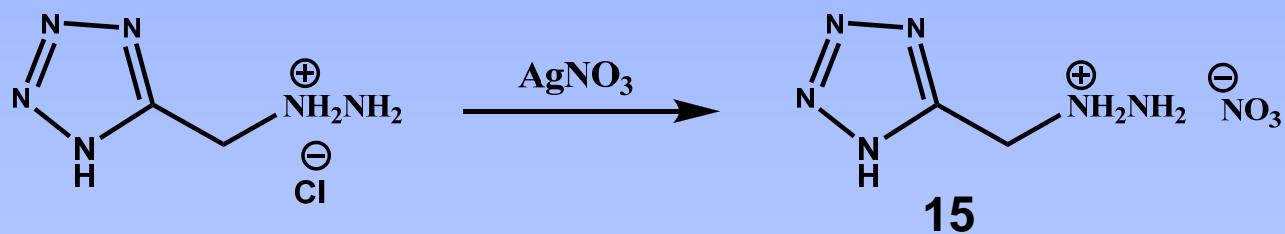
## DSC and $^1\text{H}$ NMR spectrum of 5-(hydrazino-methyl)tetrazole



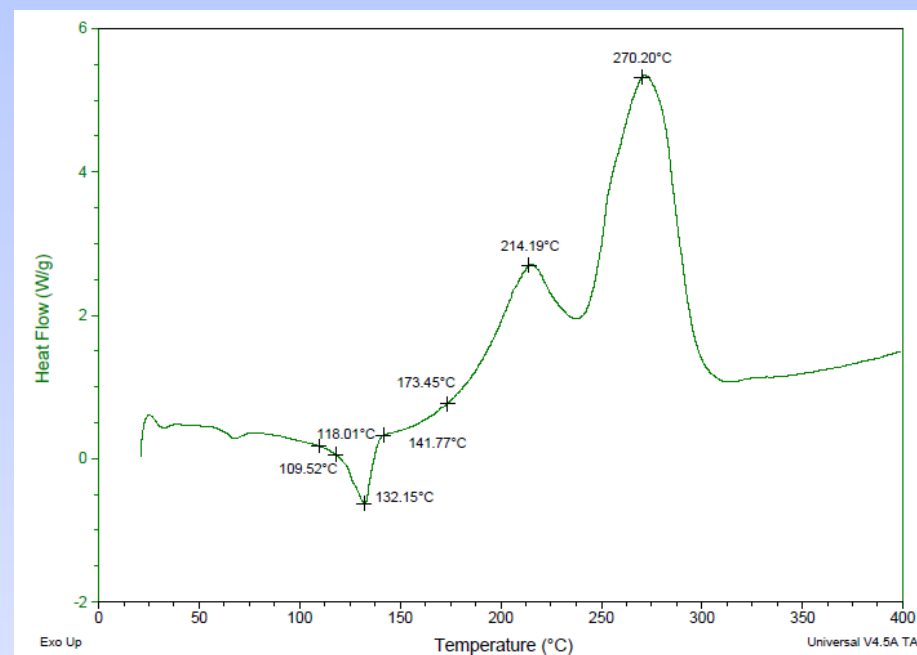
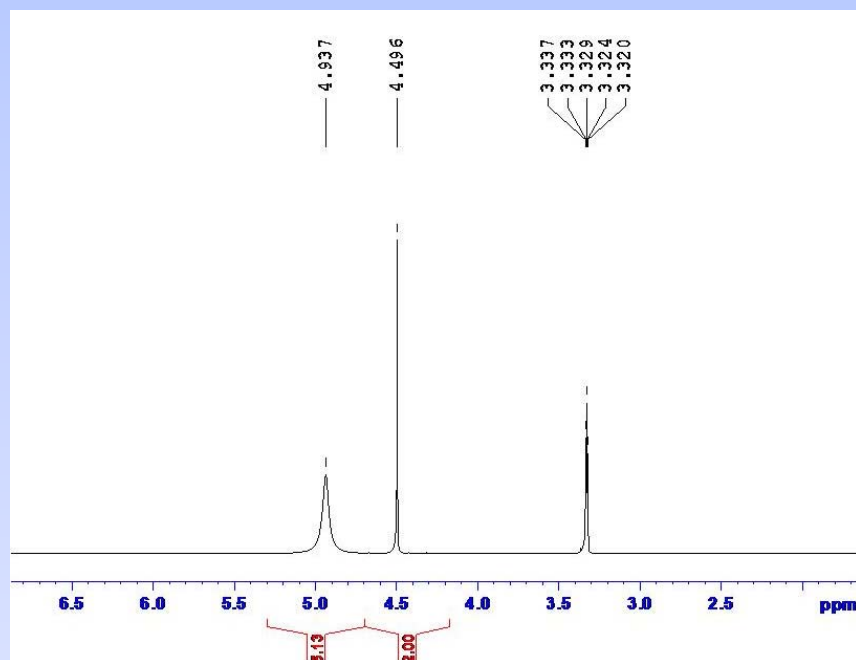
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## Metathesis reaction of 5-(hydrazino-methyl)tetrazole mono-hydrochloride with silver nitrate

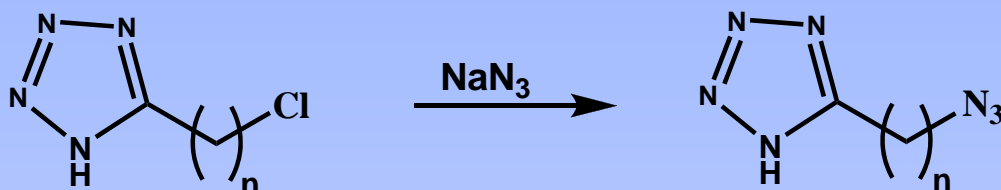


### $^1\text{H}$ NMR and DSC of 15





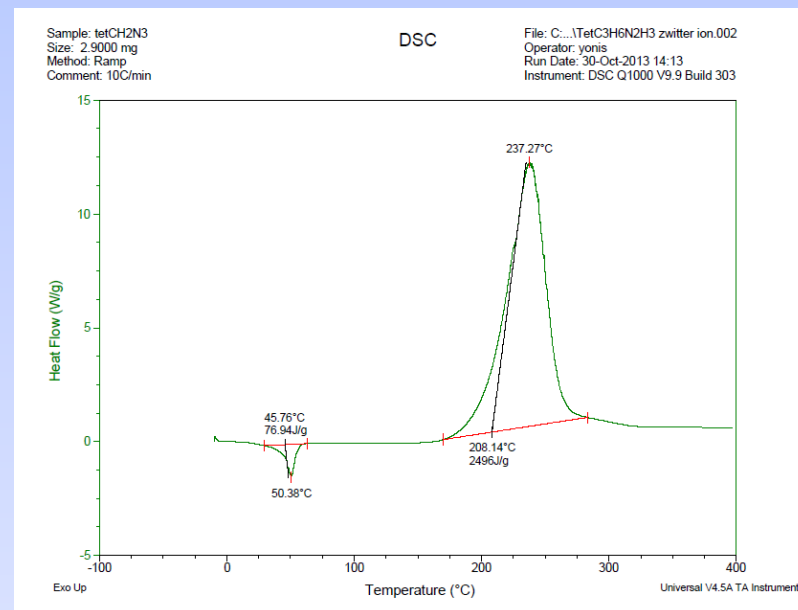
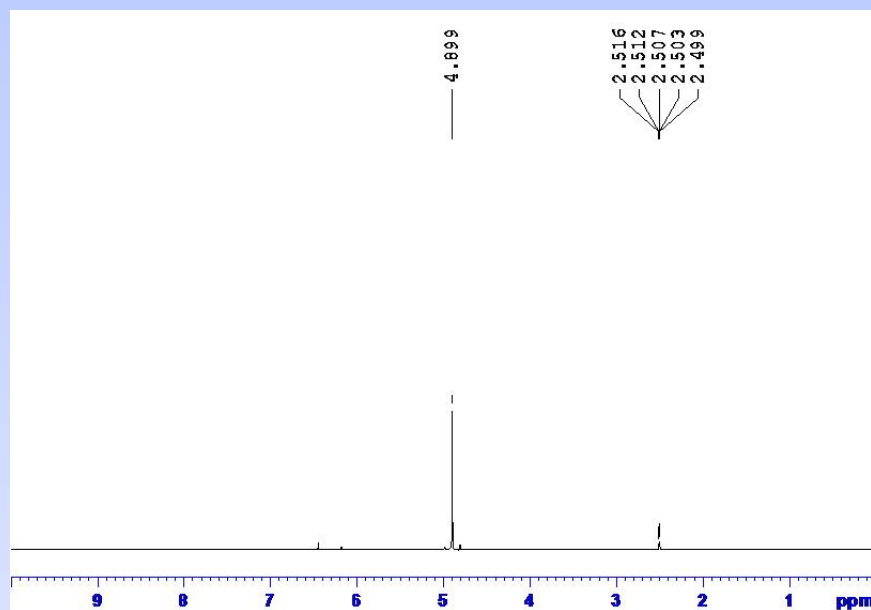
## Synthesis of 5- (azido-methyl) tetrazole



16,  $n = 1$

17,  $n = 2$

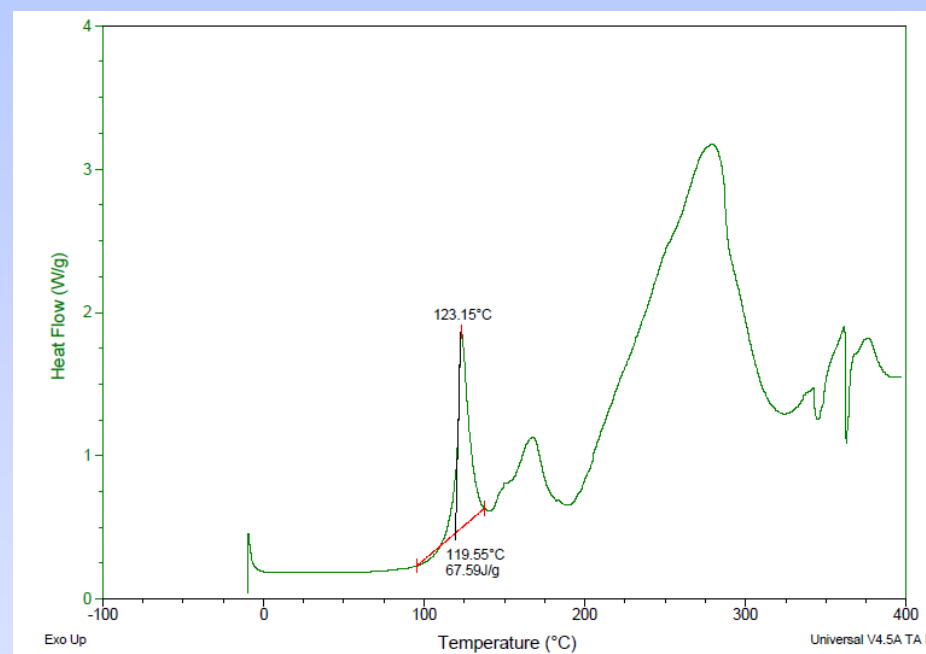
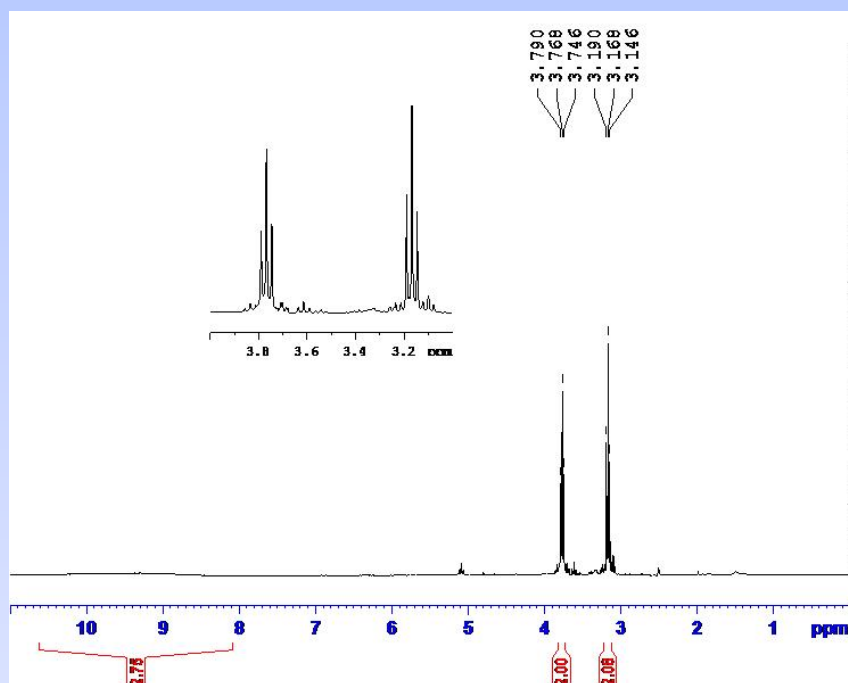
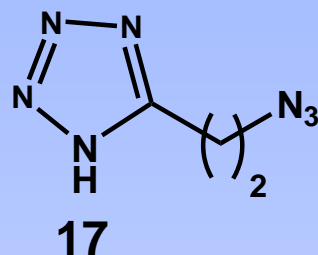
### *1*H NMR and DSC of 5-(azido-methyl) tetrazole



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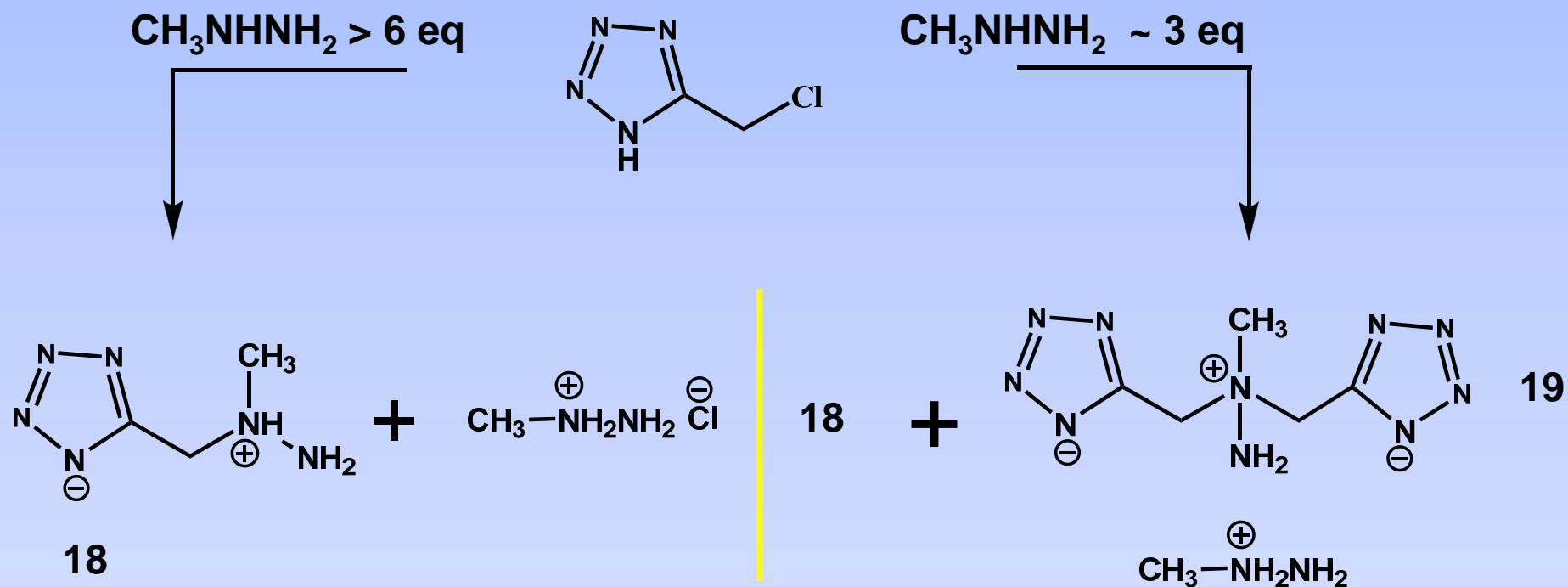
## *DSC and $^1\text{H}$ NMR spectrum of 5-(azido-ethyl) tetrazole*



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## Reaction of 5 - (chloro-methyl) tetrazole with mono-methyl hydrazine (MMH)





## *Conclusion*

- ☐ Successfully synthesized several 5-(hydrazino alkyl) tetrazole
- ☐ Fairly stable,  $T_d > 150$ , and difficult to work with due poor solubility
- ☐ Bicyclic tetrazole derivative formed via intramolecular cyclization
- ☐ Generated energetic nitrate salt and tetrazole-alkyl azides from reaction intermediates
- ☐ Reaction of MMH with 5-chloromethyl tetrazole also leads to di-alkylated derivative depending on concentration of MMH





## *Acknowledgement*



\$\$\$\$: Michael R. Berman, Ph. D., AFOSR



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**AFRL**



**ERC**

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**Christina Franquera, B.S**

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**Tommy Hawkins, Ph.D.**

**Andrew Beauchamp Capt, M.S**

**Jeff Mills, Ph.D.**

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